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Stereochemistry of Organic Compounds IV

Solvent Effects of Carbohydrate C-Nitroalcohols

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有機化合物の立体化学 Ⅳ
1-Deoxy-1-nitroheptitol の溶媒効果

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概　　要

これまで，種々の糖類，オキシ酸の nitrate を合成し，ニトロ基が旋光分散上，すぐれた発色団であることを示してきた（例えば，K. Satsumabayashi *et al.*, *Bull. Chem. Soc. Japan*, **39**, 761 (1966); **42**, 1052 (1969)). これらの化合物は殆んどの場合環状で，安定な rotamer は比較的たやすく求められるが，flexible な系においての優位コンホメーションを求めることは容易でない。

ここでは，ガラクトースにニトロメタンを作用させて，炭素数7の鎖状ポリアルコールの末端の炭素にニトロ基を持った 1-Deoxy-1-nitroheptitol を合成し，flexible な構造をもつ化合物の優位コンホメーションを調べた。化合物ⅠとⅡはエピマーであり1分子中に5個のアシメ炭素をもつが，ニトロ基に最も近い C_2^* の配座が Cotton 効果の符号を決定する。280 nm 辺の $n \rightarrow \pi^*$ 遷移に基ずく Cotton 効果はすでに佐藤ら (C. Satoh *et al.*, *Carbohyd. Res.*, **5**, 140 (1967)) によって報告されている通り C_2^* の Chirality が S のとき正，R のとき負であることが確認された。更に，本研究では NO_2 の $\pi \rightarrow \pi^*$ 遷移による Cotton 効果も 200～210 nm 辺に観測された。この符号は Chirality が R のとき正，S のとき負となる。

ついで，flexible な構造には溶媒効果が期待されるので，極性の大きい水と，極性の極めて小さいジオキサン中で，その CD, RD, UV を比較検討した。その結果極性溶媒の水溶液中で $n \rightarrow \pi^*$ 遷移は RD, CD, UV 共に blue shift することが判った。更に，CD 曲線上 302 nm (I), 307 nm (II) にある Cotton 効果が，非極性溶媒ジオキサン中では消失することが判った。これは IR でも確認された分子内水素結合が原因であり，溶媒の

影響の小さいジオキサン中での分子の conformation を決めるものである。ニトロ基の2つの O 原子は n_s 及び n_a 軌道を形成し，$n \rightarrow \pi^*$ 遷移は2つに分かれるが，1つの O 原子が分子内水素結合によって固定された Conformer では，$n_a \rightarrow \pi^*$ 遷移のみが許され，これが活性となって1つの Cotton 効果となると考えてよい。

Stereochemistry of Organic Compounds IV[1]

Solvent Effects of Carbohydrate C-Nitroalcohols

It is reported[2] that the rotatory dispersion (RD) and circular dichroism (CD) spectra of carbohydrate C-nitroalcohols exhibit a single Cotton effect due to the $n \rightarrow \pi^*$ transition of the nitro group in the wavelength region of 270 nm. On the other hand, it is reported[3] that the ultraviolet absorption (UV) spectra of some aliphatic nitro-compounds have absorption bands not only at 270 nm but below 200 nm, but no information on the rotatory contribution could be obtained concerning the latter.

In this paper, further investigations of the 270 nm Cotton effects were carried out and the 200 nm strong Cotton effects were discussed. Furthermore, since it is expected to have solvent effects in the flexible system, the correlation between conformations and behavior in the polar and non-polar solvents will be sought. For that purpose the following two compounds were synthesized, namely:

1-Deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol (Compound I) and,

1-Deoxy-1-nitro-D-*glycero*-L-*gulo*-heptitol (Compound II).

Results and Discussion

The CD, RD and UV curves and the structural formula of compounds are shown in Figs. 1 and 2. These compounds were obtained by the reaction of D-galactose with nitromethane. All curves in Figs. 1 and 2 were obtained in an aqueous solution, and their spectral data are summarized in Table 1. A regularity was found by Satoh et al.[2] When the chirality of the C_2 which is the nearist asymmetric carbon to a nitro group is *S*-configuration, the sign of Cotton effect shows positive, and in the case of *R*-configuration, the sign of Cotton effect shows negative. In the CD curve of the compound I, a large negative extreme appeared at 213 nm besides positive extremes around 280 nm. In the case of the compound II, a large positive CD maximum appeared at 203 nm in Table 1. As is clear from the UV curves, the compounds I and II exhibit absorption maxima at 201 nm and 195 nm respectively.

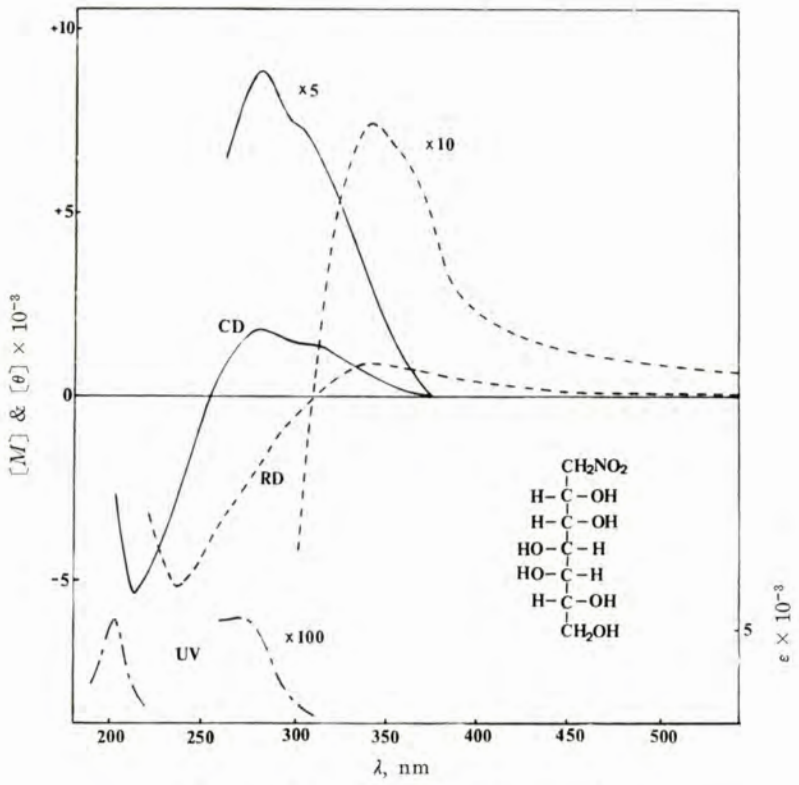

Fig. 1 RD, CD and UV of Compound I

Table 1 CD, RD and UV Data of I and II (in H_2O, $c \fallingdotseq 0.1$)

	Compound I			Compound II		
	CD $[\theta]$ (λ, nm)	RD $[\alpha]$ (λ, nm)	UV ε (λ, nm)	CD $[\theta]$ (λ, nm)	RD $[\alpha]$ (λ, nm)	UV ε (λ, nm)
$n \rightarrow \pi^*$	+1480 (302)	+ 309(P) (341)	7.50−5.80 (320−340) shoulder	−1240[1)] (307)	− 199(T) (343)	6.30−3.60 (325−340) shoulder
	+1780 (280)	−2210(T) (236)	58.9 (272)	−1370 (283)	+1730(P) (226)	54.2 (273)
$\pi \rightarrow \pi^*$	−5550 (213)	−2210(T) (236)	5740 (201)	+7190 (203)	+1730(P) (226)	5850 (195)

P: Peak T: Trough

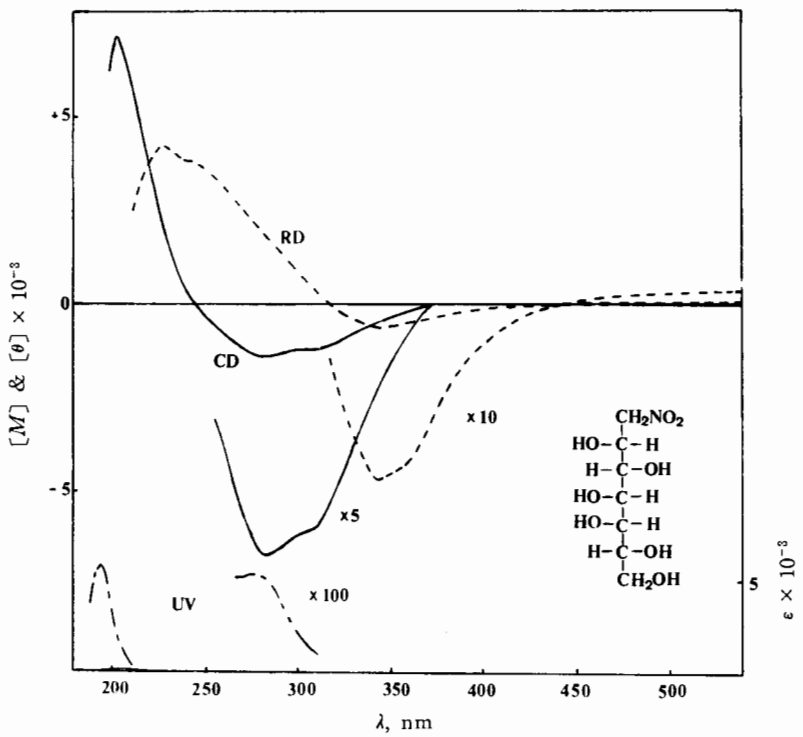

Fig. 2 RD, CD and UV of Compound II

As may be seen from the values of ε in Table 1, they are due to the $\pi \rightarrow \pi^*$ transition of the nitro group.[3,4] The $\pi \rightarrow \pi^*$ transition band of nitro group was observed on the ultraviolet absorption spectra, but was not recognized as an optically active absorption.[5] In this investigation, the $\pi \rightarrow \pi^*$ transition exhibits optically active in both the CD and the RD curves.

Now, we discuss another band of $n \rightarrow \pi^*$ transition which is seen at 302 nm for the compound I, and at 307 nm for the compound II on CD curves in water. This long-wave length band of the $n_s \rightarrow \pi^*$ of nitro chromophore is recognizable by the shoulder around 320–340 nm in the UV spectra, as well as by the same sign as the main Cotton effect due to the $n_a \rightarrow \pi^*$ transition at 283 nm.

Hereupon the authors have investigated solvent effects on RD, CD and UV. Figures 3 and 4 show the solvent effects of the compounds I and II in water as a polar solvent and in dioxane as a nonpolar solvent. As seen in Figs. 3 and 4, the $n \rightarrow \pi^*$ band shows the solvent effects clearly. The $\pi \rightarrow \pi^*$ band could not be observed, because of the absorption of dioxane itself. As the solvents become less polar, the $n \rightarrow \pi^*$ band center moves to the red,[6,7] as seen in Figs. 3, 4 and Table

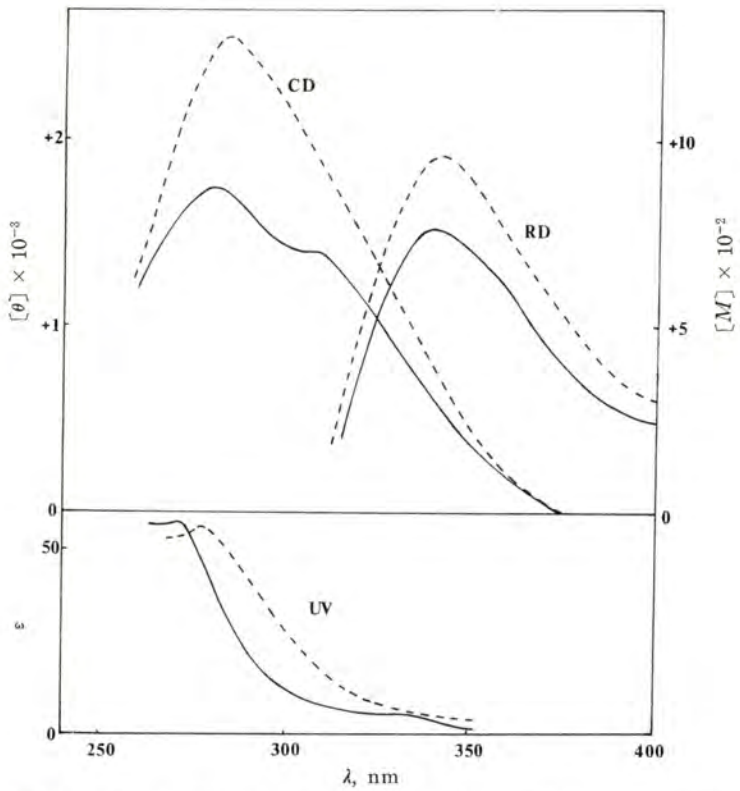

Fig. 3 RD, CD and UV of Compound I (—— H_2O, ---- dioxane)

Table 2 Solvent Effects of the $n \rightarrow \pi^*$ band ($c \fallingdotseq 0.05$)

Comp.	Solvent	CD_{max} $n_s \rightarrow \pi^*$ [θ] (λ, nm)	CD_{max} $n_a \rightarrow \pi^*$ [θ] (λ, nm)	RD [M] (λ, nm)	UV ε (λ, nm)
I	Water	+1480 (302)	+1780 (280)	+744(P) (341)	58.9 (272)
	Dioxane	——	+2580 (283)	+959(P) (343)	56.9 (277)
II	Water	−1240 (307)	−1370 (283)	−480(T) (343)	54.2 (273)
	Dioxane	——	−1490 (289)	−463(T) (344)	50.4 (278)

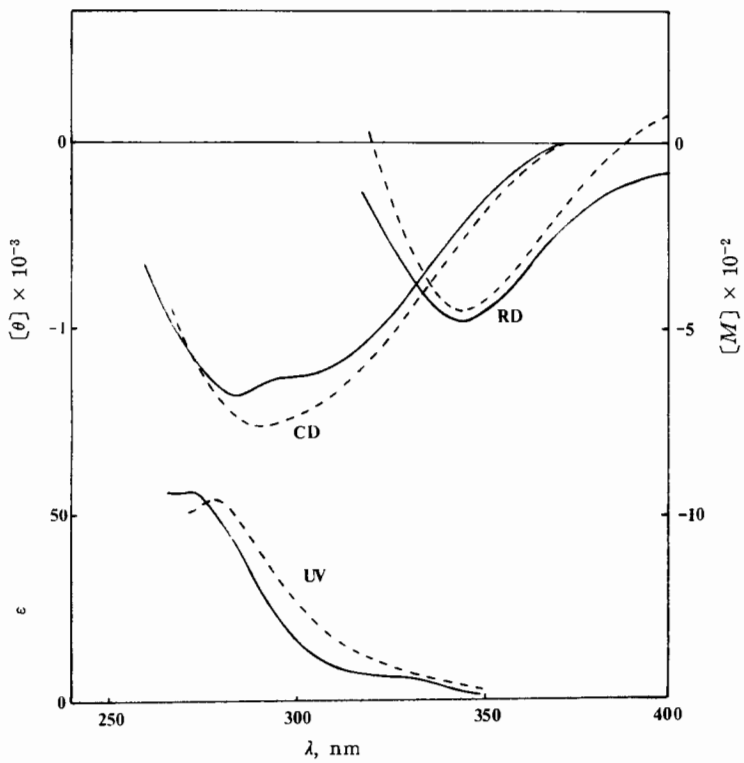

Fig. 4 RD, CD and UV of Compound II (—— H_2O, ---- dioxane)

2. On the other hand, the CD extreme of the $n_s \rightarrow \pi^*$ band disappears in dioxane solution. These results show that an oxygen atom of the NO_2 group is fixed by the intramolecular hydrogen bonding and, as a result, the orbital of nonbonding electrons of an oxygen will be observed, and only the $n_a \rightarrow \pi^*$ band of the other oxygen will occur. The rotamer, of which the nitro group is oriented to in forming the intramolecuar bonding, is rigid compared to the molecule in water. The more rigid the structure is, the more the optical contribution increases. Therefore, the value of the CD extreme in dioxane is larger than the value in water. The intramolecular hydrogen bonding was also confirmed by IR spectra. IR spectra of I and II in dioxane showed an intramolecular hydrogen-bonded NO_2 absorption around 1630 cm^{-1} at the same concentrations as those for CD measurements.

Experimental

1-Deoxy-1-nitro-D-*glycero*-heptitols I and II were prepared[6] by an additional

reaction of nitromethane to D-galactose, in the presence of sodium methylate as a base catalyst. Since a new asymmetric center was created at C_2, two stereoisomeric epimers were separated by fractional crystallization.

The infrared spectra were measured in a potassium bromide disc using a JASCO IRA-2 type diffraction grating spectrophotometer at room temperature. The rotatory dispersion and circular dichroism were measured in water and dioxane at 24.5−25°C in the wavelength from 200 to 600 nm with a JASCO ORD/UV-5 type optical rotatory dispersion recorder. The ultra-violet absorption was measured with a Hitachi 320 type spectrophotometer at room temperature. The results are shown in Tables 1 and 2.

1-Deoxy-1-nitro-D-*glycero*-L-*manno*-heptitol (Compound I). White needles; mp 148-154 °C. $[\alpha]_D^{23.5}$ + 3.11° in H_2O (*c* 0.5652).

1-Deoxy-1-nitro-D-*glycero*-L-*gulo*-heptitol (Compound II). White needles; mp 152-153 °C. $[\alpha]_D^{20}$ + 8.38° in H_2O (*c* 0.9984).

Those specific rotations were measured with a Lippich's polarimeter using a sodium lamp as the light source. The length of the layer was 1 dm.

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